MIXED WASTE FOCUS AREA TECHNOLOGY PROFILE

Molten Salt Oxidation

Who Should Read This Technology Profile?

This technology profile will be of interest to anyone responsible for the disposal of hazardous and low-level mixed wastes (LLMW) which are in the form of organic liquids or sludges. This technology is also expected to work well on organic solids with maximum dimension on the order of 6 mm (for injection purposes). Candidate DOE mixed waste streams for Molten Salt Oxidation (MSO) treatment include: spent solvents, oils, and other organic liquids; crucible graphite; plutonium contaminated leaded gloves; ion exchange resins; and energetic materials (explosives, propellants, and pyrotechnics). This technology will also be of interest to those responsible for the disposal of chemical warfare agents and medical wastes.

What is the Molten Salt Oxidation Process?

Molten Salt Oxidation is a thermal means of completely oxidizing (destroying) the organic constituents of mixed and hazardous waste. The flameless reaction takes place at 700 to 950°C in a pool of benign salts, which is usually either sodium carbonate or a eutectic of alkali carbonates (see Figure 1). Oxidant air is added with the waste stream into the salt bath, and the reaction takes place within the salt bath virtually eliminating the fugitive inventories found in incineration. The organic components of the waste react with oxygen to produce CO_2, N_2, and water. Halogens and heteroatoms such as sulfur are converted to acid gases, which are then "scrubbed" and trapped in the salt in forms such as NaCl and Na_2SO_4. Other incombustible inorganic constituents, heavy metals and radionuclides are held captive in the salt, either as metals or oxides, and are easily separated for disposal.

How Mature is the Technology?

Molten salt technology is not new. Rockwell used the process approximately 20 years ago for coal gasification. During that period, they also demonstrated the effectiveness of molten salt for destroying hazardous organics such as PCBs and TCEs. Extensive experience on laboratory-, bench–, and pilot-scale MSO units has been obtained at ETEC, LLNL, ORNL, and Rockwell since the technology's introduction. Recently, molten salt been demonstrated as an effective method for the destruction of mixed waste oils and energetic materials. The technology is mature enough to be implemented into a pilot-scale unit in the next one to two years.

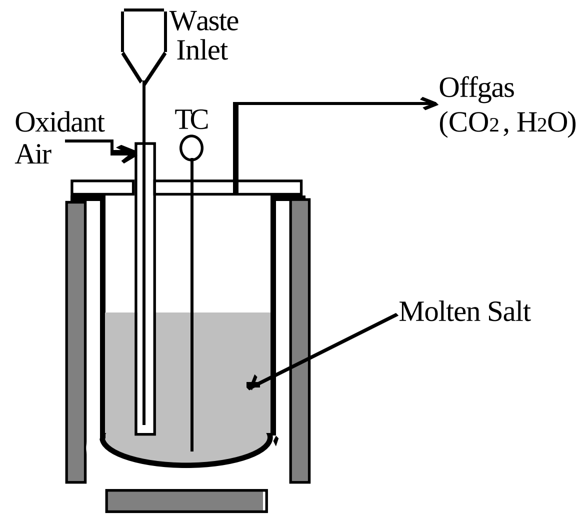

Figure 1: Schematic of the MSO Vessel

What is the Implementation Configuration?

There appear to be no obstacles to the scale-up and use of MSO as an alternative to incineration for the waste streams described in the first section; in fact, this technology will be demonstrated at the pilot scale in LLNL's Mixed Waste Management Facility (see "What is the Facility Status for Implementation of the Molten Salt Process?"). In many respects this process has advantages over incineration. The large thermal mass of the molten salt provides a stable heat-transfer medium that resists thermal surges and ensures temperature uniformity and is therefore able to tolerate rapid process fluctuations. Flame-outs are completely avoided, since MSO is a non-flame process that proceeds by catalytic liquid-phase oxidation reactions. MSO generates less off-gas than incineration, since it does not require supplemental fuel to sustain a flame. Operation of the MSO system is at temperatures hundreds of degrees lower than flame combustion temperatures, which, among other things, minimizes emissions of the radioactive materials from mixed wastes. Acid gases are "scrubbed" by the alkali salts, eliminating the need for a wet off-gas scrubbing system. Also, permitting the MSO process should be easier since it is not an incinerator; permits for the construction and operation of incinerators are difficult to obtain, and public opposition to incinerators can be strong.

What are the Operational Characteristics?

Molten salt units have been built and operated in sizes ranging from a few grams per minute to over a ton per day. Currently operational bench-scale units at ORNL and LLNL have the capacity of 500 g/hr. The pilot-scale unit currently being designed for implementation in the Mixed Waste Management Facility will have the following throughputs: 20 kg/hr for chlorinated organic liquids (DOE Waste Code 2210); 10 kg/hr for combustible solids (DOE Waste Code 5440); 6 kg/hr of non-halogenated organic liquids (DOE Waste Code 2220); 6 kg/hr for scintillation cocktails (DOE Waste Code 6140); and 5 kg/hr of Trimsol oil (DOE Waste Code 2120).

Can the Molten Salt Process be Integrated into a Complete Waste Processing System?

The MSO process is compatible with extensive use of standard industrial equipment, although the reactor vessel and feed injection system are uniquely designed and not off-the-shelf items.

What is the Facility Status for Implementation of the Molten Salt Process?

The Mixed Waste Management Facility (MWMF) is a national demonstration test bed that will be used to evaluate, at pilot scale, emerging technologies for the effective treatment of low-level radioactive, organic mixed wastes. The primary objective of the MWMF is to demonstrate integrated mixed-waste processing technologies. The demonstration will stress process scale-up to near full scale, so as to qualify each integrated process for full-scale plant operation. By integrated demonstration, we mean that all aspects of a particular treatment approach are to be demonstrated. This will include state-of-the-art waste characterization, sorting, and feed preparation technologies; waste treatment; off-gas and product waste treatment; and the preparation of robust solid final forms. Over twenty technologies were evaluated for potential demonstration as the primary treatment processes in the MWMF, and MSO was chosen as the true incineration-alternative technology. The MWMF, which will be build at LLNL, is scheduled to complete Title I in July 1995, with demonstration of MSO scheduled for FY98 (see Figure 2).

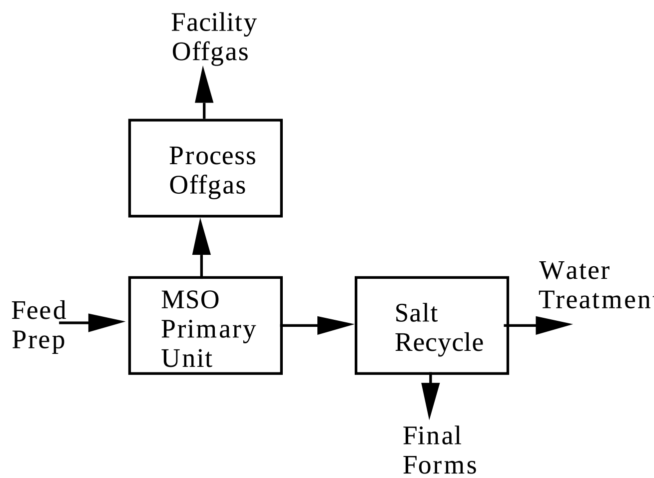

Figure 2: Flow Diagram of MSO in MWMF

What are the Technology Limitations?

Waste streams which have low heating-value materials, such as soils, decontamination and decommissioning rubble, and high-water content streams, are by themselves not practical for treatment with MSO. Some wastes, such as aqueous streams, may be suitable if additional wastes with higher heat-contents are injected simultaneously. Highly heterogeneous wastes may utilize MSO in conjunction with thermal desorption; the organic stream evolved during thermal desorption may be sent through MSO to remove all the volatiles from the off-gas.

MSO requires salt recycle for high ash waste streams or for waste with very high chloride content. High concentrations of ash lead to increases in salt melt viscosity, which may adversely affect destruction efficiency. Similarly, high chloride levels in the salt can lead to increased carbon monoxide emissions. These problems can be mitigated by changing out the salt, but without salt recycle a high volume of waste would be generated from the process – in some cases exceeding the volume of waste injected. However, with the addition of salt recycle capability, these issues will be resolved and high-ash/high chloride streams can also be easily treated by MSO.

Because of the method of waste injections, solids must be size-reduced prior to destruction via the MSO process to nominally 6 mm. An independent vendor has demonstrated the ability to size-reduce surrogate waste (booties, latex gloves, rags, plastic pipes and bottles, and glove port covers) using a knife shredder with a 1 mm screen with off-the-shelf equipment.

What are the Pros and Cons Compared to Alternate Technologies?

MSO has several advantages over incineration. First, since MSO units operate at much lower temperatures, generation of NO_x is greatly reduced, as is the volatilization of heavy metals and radionuclides. Second, the generation of acid gas is eliminated since the acid gases (such as HCl, SO_2, etc.) are scrubbed by the alkaline carbonates, producing instead water (steam) and the corresponding salt. This eliminates the need for a wet-scrubber in the off-gas system. Third, the formation of secondary toxins (dioxins, furans, and other products of incomplete combustion) are less likely with MSO. In an incinerator, hot spots and feed inhomogeneities limit the process controllability. MSO provides a stable heat-transfer medium with sufficient thermal mass/ inertia to resist thermal surges, ensuring temperature uniformity, and provides increased and uniform contact time/residence time of the primary reactants, ensuring completeness of reaction. Lastly, less off-gas is generated in MSO because there is no fuel required to sustain or initiate a flame in this process. The off-gases from MSO are sent through standard dry off-gas clean-up equipment (bag filters or HEPA filters) to remove any remaining salt particles before undergoing gas analysis and release to the atmosphere, similar to the removal of flyash from incinerator off-gas. Even with the possible addition of a soot-blower to remove salt particulates from the off-gas stream, the lower volume of off-gas makes MSO's off-gas system smaller and less cumbersome.

MSO units are more costly than incineration units. However, due to public pressure, existing incinerators are being scrutinized and are being forced to install more control and abatement devices. This increases their costs, narrowing the gap between the cost of the molten salt unit and incinerators. Public acceptance of incinerators is down, and, in fact, EPA has made the statement that it will not be accepting new incinerator permits for the next two years. Since MSO is not an incineration process, it should gain better public acceptance than an incinerator.

The disadvantages of MSO were identified in the "limitations" section above.

What are the Requirements for Commercial Use?

The key requirement for commercialization of molten salt oxidation as a waste treatment technology is the acceptance of MSO as the BDAT (Best Demonstrated Available Technology) for the treatment of mixed waste, or the determination that MSO is equivalent to BDAT for the treatment of mixed wastes. The MSO process will be permitted and demonstrated through the MWMF, which should resolve this issue.

What is the Commercial Availability of the Molten Salt Oxidation Process?

As a means of destroying organic materials, MSO is attracting industrial interest in three areas: mixed waste, medical waste, and demilitarization. LLNL is seeking industrial partners for the development and commercialization of molten-salt systems specially tailored for each waste stream of interest; partnerships are currently being formed in connection with the MSO unit in the MWMF.

What Independent Reviews of the Technology Have Been Conducted?

Two independent reviews of MSO have been conducted. In November 1991, a peer review process was conducted and facilitated by DOE Grand Junction Projects Office through its prime contractor, Chem-Nuclear Geotech, Inc., to establish a baseline evaluation of the MSO technology and to establish its present and potential readiness to treat DOE wastes. The second review was conducted in December 1993 by a panel of eight independent technical and program management experts to conduct a technical review of the technology's attributes and to determine if the technology was sufficiently promising as an alternative to incineration to be advanced to a pilot plant stage.

What are the Key References Where Additional Information Can be Obtained?

"Evaluation of the Molten Salt Oxidation Process Technology," Chem-Nuclear Geotech, Inc., DOE/ID/12584-97 GJPO-105, prepared for the US-DOE Office of Environmental Restoration, January 24, 1992.

"Technical Review of Molten Salt Oxidation," Office of Technology Development (EM-50), prepared for the US-DOE Office of Environmental Restoration, December 1993.

L. Abbey, M. McDowell, A. Darnell, R. Gay, K. Knudsen, and C. Newman, "Final Report for Molten Salt Oxidation of RMDF Mixed Wastes," 022-TR-0002, Energy Technology Engineering Center, Canoga Park, California, October 15, 1993.

P. A. Haas, J. C. Rudolph, and J. T. Bell, "Molten Salt Oxidation of Mixed Wastes at the Oak Ridge National Laboratory," ORNL/TM-12765, Oak Ridge National Laboratory, Oak Ridge, Tennessee, August 1994.

R. B. Hershey, "Mixed Waste Management Facility Conceptual Design Report," UCRL-PROP-116761 L-17293-1, Lawrence Livermore National Laboratory, Livermore, California, April 29, 1994.

A. E. Stewart, S. J. Yosim, A. J. Darnell, and R. L. Gay, "Preconceptual Design of a Closed Molten Salt Destruction System for Mixed Waste," ETEC-90-4, Energy Technology Engineering Center, Canoga Park, California, July 24, 1990.

R. D. Streit and M. G. Adamson, "Mixed Waste Management Facility Technology Selection and Implementation Plan Part I: Primary Processes," UCRL-ID-116210 Pt 1, Lawrence Livermore National Laboratory, Livermore, California, January 1994.

R. S. Upadhye, W. A. Brummond, and C. O. Pruneda, "Destruction of High Explosives and Wastes Containing High Explosives using the Molten Salt Destruction Process," UCRL-JC-109564, Lawrence Livermore National Laboratory, Livermore, California, May 1992.

S. J. Yosim, L. G. Kellogg, and S. Sudar, "Molten Salt Destruction of HCB and Chlordane - Bench and Pilot Scale Tests," EPA-600/2-84-148, Rockwell International, Canoga Park, California, September 1984.

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How Can I Access Databases for Additional Information?

This information will be supplied later.

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